

## CHARACTERIZATION OF OIL IN THE WATER COLUMN AND ON THE SURFACE AFTER CHEMICAL DISPERSION

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### Abstract

This paper reports on the analytical results of oil composition changes during the chemical dispersion process. A new gas chromatography technique is used to study oil in the water column and that residing on the surface.

The concentrations of the higher alkanes ( $C_{18}$  and above) are somewhat lower in the dispersed oil than in the starting oil and in the surface oil. This shows that these components are less dispersable than the shorter alkanes and are concentrated in the undispersed surface layer.

The overall effect of this selectivity is thought to be relatively insignificant upon the final dispersion effectiveness. The n-alkane fraction content in the surface oil shows an enrichment of higher-molecular weight compounds.

The implications of these findings are that the heavier component of oil ( $C_{24}$ - $C_{30}$ ) are only slightly less dispersable than the lighter ones ( $C_{10}$  -  $C_{18}$ ). This is suggestive that the main reason for dispersant effectiveness decrease with weathering is the loss of the highly dispersable small aliphatics ( $<C_{10}$ ) which are lost through evaporation.

### Introduction

This study is one of a continuing series exploring dispersant effectiveness and behaviour. One of the outstanding issues with dispersants is to find specific causes for the effectiveness decreases as an oil weathers. Some have suggested that this is due to the increasing viscosity and thus decreased mixing with the dispersant. This can be discounted by performing the effectiveness testing on dispersants pre-mixed with oil. Others have suggested that this is a result of the increased viscosity of the oil resulting in a larger particle size. Studies of particle sizes have shown that this is probably not the case (Fingas et al, 1995). It appears likely that the effectiveness differences may be entirely the result of a decreasing effectiveness with increasing molecular size. As oil weathers (evaporates) the remaining components have a significantly increased molecular size. This study is specifically designed to examine the differential effectiveness of dispersants as an oil weathers, in this case Federated crude, a light Alberta crude. The amount of each component was measured in the water column and in the oil remaining on the surface.

## Experimental

The following are the apparatuses employed:

- New Brunswick Environmental Shaker model G27 (New Brunswick Scientific, Edison, NJ)
- Varian Cary 1 UV/VIS spectrophotometer with a 6 cell multi-cell changer and Cary software package (Varian Canada Inc., Ottawa, ON)
- 12 matched semi-micro cells (Hellma Canada Ltd., Concord, ON)
- Hewlett Packard 5890 GC/FID with Chemstation software package (Hewlett Packard, Ottawa, ON) and a fused silica DB5ms column (J & W Scientific, Folsom, CA)
- 12 - 12mm x 32mm Crimp style vials with aluminium/Teflon seals (Supelco, Mississauga, ON)
- 12 - 125 mL glass, Erlenmeyer flasks, modified with the addition of a drain spout (VWR Scientific, London, ON)
- 6 - 25 mL glass, graduated mixing cylinders and stoppers
- 6 - 125 mL glass, separatory funnels and stoppers
- 5.0 mL glass pipette
- 5  $\mu$ L to 100  $\mu$ L positive displacement pipette (Mandel Scientific Co., Guelph, ON)
- 1 mL positive displacement pipette (Mandel Scientific Co., Guelph, ON)
- 2 - digital timers
- 20 mL to 100 mL dispenser (Brinkman Instruments Canada, Rexdale, ON)
- 2 - 25 mL glass, Erlenmeyer Flask and stopper
- 66 L plastic container and cap

Reagents and Materials are as follows:

- Dichloromethane, distilled in glass grade (Caledon, Georgetown, ON)
- Pentane -195, distilled in glass grade (Caledon, Georgetown, ON)
- Fine granular salt (Canadian Salt Co., Pointe Claire, QC)
- 20 mL chemical dispersant
- 25 mL oil
- pure water (reverse-osmosis treated or equivalent)

## Sample Collection and Storage

The initial oil and container are mechanically mixed for a minimum of 2 hours prior to obtaining a working sample. Working samples are stored in 2 L high density polyethylene bottles with polypropylene screw closures (Nalgene, Rochester, NY). For dispersant testing, an aliquot is removed as needed from the working sample and stored in a glass bottle with a plastic cap (VWR Scientific, London, ON). The working sample is manually shaken prior to removing the aliquot. When not in use all samples are stored in a temperature controlled room at 15 °C. Handling of the samples is kept to a minimum to reduce the loss of volatile components from the oil. New consumable labware and reagents were used throughout sampling and analysis of the oils.

## Procedure

The Swirling Flask Dispersant Effectiveness Test was first described in Fingas et al., 1987, and subsequently several improvements have been made. A summary of the

procedures used during this study have been provided in the following paragraphs.

The test procedure involves the addition of 100  $\mu\text{L}$  of oil premixed with dispersant (oil:dispersant of 25:1) to 120 mL of artificial sea water (oil:salt water of 1:1200) in a 125 mL modified Erlenmeyer flask. The flask, termed the 'Swirling Flask Test' vessel, is designed with a drain spout at its base to permit the collection of samples from the lower portion of the water column. The artificial salt water is a 3.3% (33 parts per thousand) by weight solution of fine granular salt in deionized water. To ensure reproducibility of results, the oil and dispersant combination are analysed using two separate runs, each containing six flasks. The flask and contents are mechanically mixed via a model G27, New Brunswick Environmental gyratory shaker with a temperature controlled chamber at 20 °C (New Brunswick, Edison, NJ). A rotation speed of 150 rpm and a mixing time of 20 minutes is used to agitate the samples followed by a 10 minute settling period in which the applied energy is removed. The settling time permits larger, unstable, dispersed droplets to separate out and return to the water surface (Fingas et al., 1989b). After 3 mL of the oil-in-water phase is drained to waste, a 31 mL aliquot is collected in a graduated cylinder. A 1 mL volume is used to measure the size of the dispersed droplets. The remaining 30 mL is transferred to a 125 mL separatory funnel and extracted with 3 x 5 mL of dichloromethane:pentane (70:30) solvent mixture. During extraction a web-like emulsion forms at the solvent/water interface. For this reason only 3 of the first 5 mL of the first extract is drained from the funnel. The extracts are combined in a 25 mL mixing cylinder and then the cylinder is capped. Two techniques are used to measure the concentration of oil in solvent. These are colorimetric analysis by ultraviolet/visible (UV/VIS) spectrophotometer and chromatographic analysis of the total petroleum hydrocarbon (TPH) content using gas chromatograph and flame ionization detector (GC/FID). A description of the instrumentation and experimental parameters are given in subsequent paragraphs.

Oil remaining on the surface after the dispersion experiment is sampled with a pipette. Samples were drawn from all 12 experiments and then extracted with the 70:30 dichloromethane:pentane mixture and treated the same as the water column extracts.

A semi-micro, UV/VIS cell (Hellma Canada Ltd., Concord, ON) is filled with a portion of the 13 mL solvent extract and its absorbance measured at 340 nm, 370 nm and 400 nm. The absorbance of the samples is compared to a calibration curve derived from the absorbance of a series of prepared oil-in-solvent standards. A 900.0  $\mu\text{L}$  portion of the 13 mL solvent extract and a 100.0  $\mu\text{L}$  volume of internal standard (100 ppm 5- $\alpha$ -Androstane) are placed in a 12mm x 32mm Crimp style vial with aluminium/Teflon seals (Supelco, Mississauga, ON) for chromatographic analysis. The resulting sample chromatograms are compared to those of the aforementioned oil-in-solvent standards to determine their respective total petroleum hydrocarbon content. In turn, the TPH concentrations of the samples and standards are used to calculate effectiveness of the dispersant. The standards represent a range of percent (%) efficiency from 0% to 100%. Subsequent paragraphs provide a detailed description of the preparation of the standard solutions. The results from each of the three wavelengths are averaged for each sample. The final % effectiveness result reported is the arithmetic mean of the 12 samples.

A series of 12, oil-in-solvent standards are prepared in a manner similar to the sample analysis procedure. One hundred twenty millilitres of salt water is placed in each of the 125 mL Swirling Flask Test vessels (SFT) followed by the addition of an accurate volume of oil/dispersant to the surface of the water. The progression of oil/dispersant

volumes ranges from 2.0  $\mu\text{L}$  to 100.0  $\mu\text{L}$  representing 2% to 100% efficiency. Table 1 provides a description of the standards. As in the case of the sample analysis a 20 minute mixing time and 10 minute settling period is employed. After which the entire volume of water is extracted with 3 x 20 mL of a solvent mixture of dichloromethane/pentane. A 5 mL volume of the first extract is left in the separatory funnel due to the incomplete separation of the water and solvent layers. The extracts are combined in a cylinder to a total volume of 55 mL. Using the procedure outlined in the UV/VIS instrument manual the absorbance of each of the extracts is measured at 340 nm, 370 nm and 400 nm. A graph of percent efficiency versus absorbance is prepared for each wavelength. With the data management capabilities of the computer and software package, the absorbance of samples is automatically compared to the data from the standards to produce percent efficiency results.

Chromatographic analysis involved obtaining a 900.0  $\mu\text{L}$  aliquot from the extract of each standard and combining it with a 100.0  $\mu\text{L}$  volume of internal standard (100 ppm 5- $\alpha$ -Androstane) in a crimp-cap vial. GC/FID analysis is conducted by an auto-injection of a 1  $\mu\text{L}$  to 2  $\mu\text{L}$  volume taken from the vial. The temperature program has been described in later paragraphs. Total petroleum hydrocarbon content is quantified by the internal standard method using the baseline corrected total area of the chromatogram and the average hydrocarbon response factor determined over the entire analytical range. A calibration curve of TPH versus percent efficiency is produced. From a comparison of the calibration curve to the TPH content of the samples the percent efficiency is calculated.

Table 1: Oil-in-Solvent Standards for Swirling Flask Test

Standard #	Oil Volume ( $\mu\text{L}$ )	Water Volume (mL)	Oil to Water ratio	Solvent Volume (mL)	Efficiency (%)
1	2.0	120	1:60000	55	2
2	4.0	120	1:30000	55	4
3	8.0	120	1:15000	55	8
4	12.0	120	1:10000	55	12
5	16.0	120	1:7500	55	16
6	24.0	120	1:5000	55	24
7	32.0	120	1:3750	55	32
8	40.0	120	1:3000	55	40
9	50.0	120	1:2400	55	50
10	64.0	120	1:1875	55	64
11	80.0	120	1:1500	55	80
12	100.0	120	1:1200	55	100

A description of the instrumentation and experimental parameters follows. A maintenance and calibration schedule of the equipment is given, to ensure reproducibility and accuracy of results.

- Spectrophotometric analysis is carried out using a Cary 1 UV/VIS spectrophotometer with Cary 1 software package (Varian Canada Inc. Ottawa, ON). Measurements of the absorbance are taken at 340 nm, 370 nm and 400 nm. Operation of the instrument followed manufacturers' instructions. Semi-micro matched quartz cuvettes (Hellma Canada Ltd., Concord, ON) are used. Daily calibration of the UV/VIS spectrophotometer is carried out using a commercially available Holmium Oxide filter (Perkin Elmer, Norwalk, CT). The filter has a quantifiable absorbance at specific wavelengths over the ultraviolet and visible wavelength range. Calibration with the filter ensures proper operation of the wavelength drive. On a monthly basis, the photometric accuracy and linearity of the spectrophotometer is checked using a commercially available kit containing solutions of potassium chromate and cobalt ammonium sulphate (Oxford Labware, St. Louis, MO).
  
- Total Petroleum Hydrocarbon analysis for  $C_8$  through  $C_{40}$  n-alkanes and pristane and phytane in the dispersed oil-in-water is carried out by high resolution capillary GC/FID under the following conditions:
  - Instrument - Hewlett Packard 5890 (Hewlett Packard, Ottawa, ON)
  - Column - 30 M x 0.32 mm ID DB-5 fused silica column (0.25  $\mu$ m film thickness), (J & W Scientific, Folsom, CA)
  - Detector - flame ionization detector
  - Autosampler - Hewlett Packard 7673
  - Inlet - Splitless
  - Gases - Carrier - helium, 2.5 mL/min, nominal  
Make up - helium, 27.5 mL/min  
Detector air - 400 mL/min  
Detector hydrogen - 30 mL/min
  - Injection volume - 1  $\mu$ L
  - Injector temperature - 290 °C
  - Detector temperature - 300 °C
  - Temperature program - 50 °C for 2 minutes, then 6 °C/min to 300 °C, hold 16.7 minutes. The total run time is 60 minutes.
  - Daily calibration - Alkane standard mixture of 20 ppm (5- $\alpha$ -Androstane, Alkane mix, o-Terphenyl in hexane) is measured before and following each sample set.
  
- Prior to the start of the project a mechanical, hand-held tachometer (Shimpo DT-105, Japan) is used to measure the rotation speed of the New Brunswick Environmental Shaker. The speed control is adjusted as necessary to achieve a consistent setting of 150 rpm. As well, the interior of the sample chamber is cleaned on a bi-weekly basis.
  
- The buildup of salt deposits on the dispenser used to add the salt water to the SFT vessel affects the mechanics of the apparatus. Over time it will result in a decrease in the accuracy of the volume of water delivered. Each time the reagent

bottle is replenished with salt water the dispenser is thoroughly cleaned with deionized water. To confirm that the dispensette delivered the specified volume of salt water the following test is performed. Two, 60 mL volumes of salt water are dispensed into an appropriate graduated cylinder and the volume on the cylinder read. Adjustments to the setting of volume control are made if necessary. Delivery volume is typically  $120 \text{ mL} \pm 1 \text{ mL}$ .

- Positive displacement pipettes and air displacement pipettes, dedicated solely to this project, certified by the manufacturer and evaluated in the laboratory are used throughout the analysis. The positive displacement pipettes are used to prepare standards and internal standard solutions for GC analysis and add the dispersant to the oil and place the oil into the Swirling Flask Test vessel. Air displacement pipettes are used to withdraw the aliquot of the extract for chromatographic analysis.
- High purity solvents and reagents and certified standards are used throughout the analysis.
- A rigorous labware cleaning program is undertaken throughout the experiment to reduce possible cross-contamination. Labware is thoroughly rinsed with deionized water and dichloromethane between each experimental run. On the last working day of the week the labware is soaked in a Decon 75 solution (BDH Inc, Toronto, ON) for 24 hours, rinsed with deionized water followed by the solvent acetone. Glassware is dried at  $180^\circ\text{C}$  while plasticware is air dried.

In this series of experiments, Federated crude oil, a light oil from Alberta, was used to measure the amounts of the n-alkanes in the water column and on the surface compared to the starting oil. The oil was used as a fresh oil, 15%, 28% and 42% evaporated. Four different dispersant formulations were used, Corexit 9500, Corexit 9527, Dasic LTS and Enersperse 700. Each n-alkane peak between C8 and C30 was quantified on the basis of the internal standard.

## Results and Discussion

The gas chromatographic counts derived from the experiments are shown in Tables 1 to 4. The values in the tables under the columns marked as '#', are repeat experiments of the oil in the water column resulting from the dispersion. Values are in relative counts. For calibration purposes, an internal standard was added. The known quantities of these can be used to yield an accurate quantity of the oil in the water column. The relative counts can be, however, used independently to yield data on the differential action of dispersants. These tables clearly show that the amount of the components in the water column decrease sharply as the weathering percentage increases. Furthermore, it can be seen from the tables that there is a difference in the amount of the larger components found in the water column as a result of the different dispersants. Corexit 9500 shows the least difference in the amount of larger and smaller components dispersed.

The values of the counts were used to calculate the ratios of the amounts of the different oil compounds in the water versus that on the surface. The ratios between C10 and C12 (decane and dodecane) and C28 and C30 were averaged to yield a single value. If any of these components were absent, the next pair of carbon number values were used. The result ratios are shown in Table 5 and represent the differential in the amount

**Table 1 Results of Dispersion Tests - Fresh Federated Crude**

Dispersant - Corexit 9500				relative peak size in counts									
Carbon #	#1	#2	#3	#4	#5	#6	#7	#8	#9	#10	#11	#12	Top
C8	14304	13307	10866	11735	25749	10001	12595	24960	7379	13883	18731	21653	2146
C10	18284	18516	18201	20540	29536	17415	17729	27660	13989	18349	22332	25199	6288
C12	20795	22748	22311	25062	33044	23688	20680	29774	18094	20893	24394	28005	8851
C14	21117	23012	22188	25446	32754	23566	21060	29707	18305	20745	24179	27536	8802
C16	14984	16319	15950	18133	23331	16871	15036	21181	13127	14824	17305	19716	6335
C18	10368	11435	11204	12719	16429	11828	10474	14844	9120	10328	12067	13930	4230
C20	9705	10504	10343	11718	15121	10968	9764	13668	8492	9535	11114	12774	4088
ISTD	23229	22937	22113	23802	31666	22847	24293	33018	21537	24334	28822	29433	21264
C22	7888	8756	8527	9720	12700	9176	8170	11530	7049	7934	9196	10715	3297
C24	6227	6776	6626	7542	9872	7125	6366	9064	5691	6235	7292	8398	2558
C26	5572	6458	5954	7060	9051	6491	5783	8694	4933	5978	6698	7850	2392
C28	3575	4049	3860	4052	6029	4138	3582	5131	3176	3600	4364	4861	1466
C30	2588	2670	2561	3167	4223	2871	2899	3877	2445	2929	3091	3689	1042

Corexit 9527													
Carbon #	#1	#2	#3	#4	#5	#6	#7	#8	#9	#10	#11	#12	Top
C8	1995	3528	4701	4174	4941	1895	3668	2672	3632	7320	3234	4794	6613
C10	2207	4446	4478	4740	5667	3118	4206	4525	4568	7739	4285	5710	13433
C12	3709	5072	5160	4706	6313	4194	5197	6254	4889	7514	4844	5606	14022
C14	3757	5939	5344	4187	5430	3317	4666	5567	5108	6964	3903	6124	13489
C16	2821	3858	3838	3857	4897	3010	4338	5066	3689	6142	3547	4398	8261
C18	127	-12	46	10	929	81	237	399	807	818	304	1078	4844
C20	1254	1935	1891	1914	2499	1303	2218	2613	1913	3254	1879	2338	6293
ISTD	31399	39500	45159	42729	46599	29775	43925	33799	34231	48944	34280	35505	41053
C22	1089	1722	1718	1762	2218	1263	1907	2260	1634	2860	1637	2035	5003
C24	798	1463	1388	1338	1706	936	1480	1740	1300	2227	1275	1627	4229
C26	662	1241	1230	1226	1570	892	1273	1517	1168	2008	1207	1428	3770
C28	450	894	1055	680	1064	449	747	1018	704	1393	822	659	2432
C30	-	475	544	535	731	-	404	495	476	843	413	596	1689

Dasic LTS													
Carbon #	#1	#2	#3	#4	#5	#6	#7	#8	#9	#10	#11	#12	Top
C8	1860	2596	1354	1446	2973	1994	3344	3206	2350	2308	2029	1570	1477
C10	2607	3836	1422	1953	3501	2043	3742	3460	2847	2431	2132	669	18649
C12	4930	5248	2542	3852	5762	3638	5387	4166	4908	3653	3870	3134	19906
C14	5149	4994	3101	3945	6008	4412	5501	3903	4961	3617	4124	3113	19576
C16	3213	3199	1456	2472	3631	2257	3530	2441	3129	2234	2599	2667	12864
C18	1425	1816	648	1321	2219	824	1499	1347	1810	1217	1023	532	8377
C20	2401	2243	1131	1871	2826	1751	2625	1852	2396	1698	1945	1439	9016
ISTD	39944	31347	32172	35586	46705	48467	47073	46856	48426	40604	40601	38794	179
C22	2034	1615	932	1523	2278	1508	2227	1559	1819	1289	1665	1038	7793
C24	1487	1377	702	1134	1852	1138	1634	1243	1525	1075	1238	926	5901
C26	1207	1177	429	949	1623	776	1268	1058	1211	924	1065	778	5326
C28	858	859	337	677	1121	687	913	904	758	463	568	512	3183
C30	589	546	-	317	761	381	526	437	518	372	442	302	2234

Enersperse 700													
Carbon #	#1	#2	#3	#4	#5	#6	#7	#8	#9	#10	#11	#12	Top
C8	762	2163	1139	684	3067	1687	1565	1152	1861	2078	2629	1488	12257
C10	730	2745	136	744	3556	733	2120	1630	2362	2690	3261	492	20873
C12	1982	3377	2589	2028	4069	3734	3014	3017	3616	3375	4239	2664	23682
C14	1827	3231	2417	1915	3864	3477	3109	2929	3430	3861	4077	2379	23690
C16	815	2766	2080	1668	2237	1964	2632	1633	1961	1774	2392	1323	15564
C18	192	689	338	454	1261	1050	600	805	974	991	952	707	10638
C20	718	1366	1023	819	1711	1517	1348	1245	1538	1398	1818	1067	10802
ISTD	21007	35016	25115	23194	38488	35366	32593	30128	32994	35792	36133	25405	38565
C22	548	1200	718	545	1227	1043	933	1027	1348	1239	1324	932	8730
C24	419	896	633	501	1083	906	816	751	981	861	1185	727	7029
C26	378	805	433	430	937	677	690	663	875	755	1067	675	5831
C28	-	507	221	268	578	367	276	459	376	542	762	485	3678
C30	-	296	-	-	295	275	280	261	325	311	472	236	2583

- Numbers in columns refer to repeat analysis of water column samples
- Top refers to analysis of oil remaining on surface after dispersion experiment
- ISTD is the internal standard

**Table 2 Results of Dispersion Tests - Federated Crude - 15% Evaporated**

Dispersant - Corexit 9500				relative peak size in counts									
Carbon #	#1	#2	#3	#4	#5	#6	#7	#8	#9	#10	#11	#12	Top
C8	8138	7751	6268	10251	5959	2083	6097	6168	5958	7992	7762	9436	354
C10	15594	15721	12940	17459	13088	6569	11726	12651	11604	13789	14033	16008	12777
C12	19205	19552	17578	20525	17470	9109	14532	16472	15145	15983	15919	18164	17444
C14	19337	20057	17819	20533	17866	9231	14694	16891	15445	16384	15756	17828	17908
C16	13784	14180	12814	14477	12666	6492	10423	11968	10947	11668	11489	12426	12294
C18	9517	9836	8843	10107	8795	4344	7116	8230	7504	7982	7806	8442	8633
C20	8908	9236	8439	9452	8227	4301	6788	7792	7182	7655	7359	8047	8165
ISTD	23923	25864	24917	25395	24486	12132	21296	22122	23469	24460	23173	23982	395
C22	7494	7723	6966	7785	6873	3544	5648	6414	5861	6321	6065	6718	6775
C24	5764	6050	5540	6150	5527	2723	4378	5032	4641	4968	4655	5291	5264
C26	5469	5555	4979	5604	4751	2434	4211	4668	4445	4841	4238	5123	4830
C28	3168	3409	3018	3680	3132	1905	2925	2878	2699	2744	2771	3278	3171
C30	2331	2633	2114	2784	1947	1158	1745	2212	1995	2013	1824	2403	2352

Corexit 9527													
Carbon #	#1	#2	#3	#4	#5	#6	#7	#8	#9	#10	#11	#12	Top
C8	880	1014	1083	1256	1294	723	1140	730	918	402	823	983	6626
C10	1525	2068	1952	2167	2116	1296	1855	1339	1935	693	1575	493	19126
C12	2329	3551	2368	2903	3116	2047	3731	1829	3125	919	1948	2985	20830
C14	3208	3837	3317	3198	3310	-	4225	-	3636	-	-	-	21017
C16	1803	2770	2264	2779	2405	1536	3157	-	2433	-	1937	2286	13137
C18	234	88	312	98	0.3	-	238	-	86	-	-	168	8184
C20	676	1153	760	762	995	601	1490	468	1113	-	610	921	9907
ISTD	37811	40034	44161	44422	48371	34804	45513	37352	42598	21423	40946	43860	462
C22	587	1054	672	882	943	622	1666	809	957	-	588	975	7681
C24	553	836	542	672	701	465	1500	445	825	-	597	919	6557
C26	479	732	498	651	789	522	790	313	819	-	309	678	5572
C28	-	451	-	366	444	-	492	-	380	-	-	433	4294
C30	-	-	-	-	-	-	-	-	-	-	-	-	2400

Dasic LTS													
Carbon #	#1	#2	#3	#4	#5	#6	#7	#8	#9	#10	#11	#12	Top
C8	211	1957	1596	2992	1465	2181	1851	2423	2160	1233	2026	2107	1236
C10	778	3898	3000	4898	1699	3724	3543	3966	3797	2003	3399	3534	22694
C12	3457	7154	5412	6342	5394	6008	6574	6669	6613	4050	5801	5979	27492
C14	3883	7599	5462	6276	5540	6179	6901	7109	7088	4405	6005	6176	27176
C16	2626	5096	3537	4053	3566	3841	4715	4663	4480	2713	3768	3915	18006
C18	1117	3092	2095	2448	2111	2287	2851	2849	2784	1068	2294	2359	12151
C20	2257	3683	2696	3110	2778	2948	3557	3563	3389	2125	2952	3202	12572
ISTD	39747	45028	39310	47405	37217	39271	48150	45757	43561	43051	46323	51320	597
C22	1754	2877	2057	2719	2362	2510	2824	2728	2882	1603	2629	2488	10154
C24	1514	2413	1776	2087	1813	1899	2307	2389	2204	1358	1959	2110	8243
C26	1352	1971	1603	1720	1612	1657	1838	2132	1778	1141	1729	1673	7476
C28	889	1476	805	991	837	1170	1467	1206	974	640	1070	1307	4269
C30	427	795	608	757	694	619	785	1044	662	422	688	683	3205

Enersperse 700													
Carbon #	#1	#2	#3	#4	#5	#6	#7	#8	#9	#10	#11	#12	Top
C8	717	729	985	686	416	665	361	468	551	294	944	542	182
C10	1580	1941	2126	1285	612	45	735	887	610	152	2454	296	9558
C12	2501	4178	3233	2331	2103	2273	3142	2262	2327	2168	3956	3315	12186
C14	2596	4498	3371	2241	2079	2279	3439	2224	2390	2061	3986	3282	12752
C16	1343	2723	1870	1234	1179	1223	2067	1286	1336	1114	2161	1900	8473
C18	583	1469	1182	646	512	608	806	595	330	589	965	656	5536
C20	1305	2075	1577	1031	948	1014	1609	1009	1073	954	1817	1526	5989
ISTD	29425	31359	30668	26247	21606	25526	25538	22891	21402	19928	32151	30465	-79
C22	926	1562	1170	829	673	699	1160	879	756	653	1552	1314	4788
C24	954	1369	1084	680	616	642	1063	684	724	633	1162	980	3954
C26	780	1014	939	570	400	557	800	533	666	477	1074	835	3415
C28	335	746	332	458	206	418	578	312	411	310	664	596	2015
C30	313	451	335	259	-	-	306	-	-	-	386	255	1573

- Numbers in columns refer to repeat analysis of water column samples
- Top refers to analysis of oil remaining on surface after dispersion experiment
- ISTD is the internal standard

**Table 3 Results of Dispersion Tests - Federated Crude - 28% Evaporated**

Dispersant - Corexit 9500				relative peak size in counts									
Carbon #	#1	#2	#3	#4	#5	#6	#7	#8	#9	#10	#11	#12	Top
C8	-	-	-	-	-	-	-	-	-	-	-	-	-
C10	4592	3891	4074	-	2738	3508	5161	4949	3061	4547	4412	3372	14401
C12	10324	10326	9898	-	6709	8463	10122	10312	7029	9722	9530	7616	31330
C14	11709	11460	11210	-	7455	9387	11076	11366	8162	11189	10366	8154	33833
C16	8344	8023	7864	-	5483	6538	7609	7868	5689	7848	7068	5702	23476
C18	5565	5416	5302	-	2998	4257	4972	5230	3760	5219	4741	3736	16514
C20	5453	5282	5170	-	4409	4199	4892	5123	3730	5200	4718	3739	15202
ISTD	41640	19696	18847	-	15635	20720	21213	21361	15857	21368	23295	18909	751
C22	4298	4325	4219	-	5848	3339	3994	4121	2985	4208	3776	3029	12340
C24	3378	3476	3268	-	4656	2518	3250	3304	2388	3347	2967	2428	9703
C26	3242	2971	2882	-	4493	2293	2951	2824	2053	2990	2677	2040	9448
C28	1784	1793	1711	-	2337	1329	1707	1776	1234	1850	1612	1209	5456
C30	1362	1288	1085	-	1888	897	1242	1212	777	1434	1250	867	4576

**Corexit 9527**

Carbon #	#1	#2	#3	#4	#5	#6	#7	#8	#9	#10	#11	#12	Top
C8	-	-	-	-	-	-	-	-	-	-	-	-	-
C10	614	969	871	303	407	212	570	542	889	236	362	296	15860
C12	1771	2285	2338	761	1164	898	1203	1222	1863	1218	1107	1009	31973
C14	2768	2839	3082	-	-	-	-	-	2263	-	-	-	34904
C16	1802	2182	2272	-	1093	-	1050	903	1756	1046	-	-	22462
C18	-394	139	229	-	-	-	-	-	-291	-	-	-	14764
C20	888	1029	1092	-	393	-	308	378	747	315	259	-	15784
ISTD	47825	46042	46422	36324	39923	31132	48016	49149	49956	48335	39434	39191	726
C22	830	1002	1087	296	427	-	386	452	819	449	474	-	12391
C24	706	828	945	-	329	-	355	365	644	289	383	-	10519
C26	624	777	695	-	366	-	328	361	547	-	180	-	8813
C28	439	468	568	-	-	-	-	-	453	-	-	-	5847
C30	-	289	315	-	-	-	-	-	-	-	-	-	3834

**Dasic LTS**

Carbon #	#1	#2	#3	#4	#5	#6	#7	#8	#9	#10	#11	#12	Top
C8	-	-	-	-	-	-	-	-	-	-	-	-	163
C10	1824	2086	1826	3412	3260	2515	1949	2990	1465	1874	1509	2829	12746
C12	5542	6261	6437	8524	7756	7649	6138	7755	4594	6409	4310	6768	24587
C14	6255	7061	7268	9388	8395	8424	7023	8746	5085	7079	4800	7140	26020
C16	4109	4631	4770	6139	5488	5513	4546	5770	3116	4617	3115	4591	17139
C18	2529	2944	2866	3897	3425	3400	2728	3587	1291	2709	1797	2720	11474
C20	3052	3534	3424	4574	4081	4115	3420	4237	2437	3440	2399	3472	12026
ISTD	37125	46936	48077	48849	53455	49513	40445	53151	37950	44808	45319	45217	56023
C22	2402	2702	2601	3556	3275	3313	2613	3570	1833	2997	1851	2617	9850
C24	1964	2288	2274	2996	2635	2717	2186	2735	1572	2294	1604	2280	8068
C26	1708	1995	1866	2690	2079	2105	1926	2415	1339	1962	1371	2019	6915
C28	916	1005	1261	1335	1261	1471	1135	1509	945	1240	875	1052	4564
C30	496	753	636	952	759	821	660	815	434	743	511	709	3136

**Energizer 700**

Carbon #	#1	#2	#3	#4	#5	#6	#7	#8	#9	#10	#11	#12	Top
C8	-	-	-	-	-	-	-	-	-	-	-	-	-
C10	1800	1862	1388	2295	1777	1515	2256	1917	1268	2004	2571	1199	-
C12	565	440	413	568	476	512	602	481	441	483	457	387	5930
C14	2340	1791	2143	2436	2657	1559	2972	2329	1917	2785	1998	1718	27231
C16	2183	1441	1278	1956	1704	1139	2306	1759	1492	1684	2396	1290	23335
C18	827	843	789	1251	925	644	1542	648	764	943	914	754	16585
C20	1296	1243	1149	1688	1484	1012	1985	1550	1264	1461	1343	1147	16613
ISTD	41784	40579	36073	50802	46585	37270	49417	40519	37535	44935	47565	37237	666
C22	938	949	853	1437	1076	880	1501	1360	897	1300	1197	1015	13487
C24	884	841	774	1104	982	679	1304	1067	813	976	864	770	10585
C26	742	610	594	939	891	500	1114	816	733	835	763	503	10229
C28	373	419	417	573	435	312	791	526	329	410	358	286	6150
C30	305	294	316	308	316	-	374	350	-	422	-	-	4223

- Numbers in columns refer to repeat analysis of water column samples
- Top refers to analysis of oil remaining on surface after dispersion experiment
- ISTD is the internal standard

**Table 4 Results of Dispersion Tests - Federated Crude - 28% Evaporated**

Dispersant - Corexit 9500													
relative peak size in counts													
Carbon #	#1	#2	#3	#4	#5	#6	#7	#8	#9	#10	#11	#12	Top
C8	-	-	-	-	-	-	-	-	-	-	-	-	-
C10	-	-	-	-	-	-	-	-	-	-	-	-	-
C12	2333	2833	2065	1866	1797	1056	2462	1283	1908	1873	1442	1529	6956
C14	9753	11871	8492	7583	7048	4131	10173	5291	7821	7794	5744	6187	29493
C16	9055	10781	7775	6973	6343	3783	9023	4774	7219	7209	5224	5655	26064
C18	6335	7757	5420	4714	4307	2515	6664	3255	5115	5007	3629	3458	18871
C20	6244	7500	5405	4849	4411	2675	6549	3388	5120	5087	3762	3953	17529
ISTD	23645	24147	22233	24812	22536	15937	23133	13260	21888	23080	22343	22350	23890
C22	5156	6211	4375	3979	3622	2050	5345	2811	4167	4136	2968	3118	14651
C24	3959	4816	3529	3203	2963	1641	4122	2227	3217	3324	2470	2627	11387
C26	3488	4476	3172	2828	2674	1581	3664	1990	2883	2916	2015	2152	10994
C28	2459	2465	1655	1521	1413	842	2094	1235	1640	1578	1224	1265	6448
C30	1388	1709	1289	1107	1002	548	1350	850	1061	1027	850	928	4771

Corexit 9527													
Carbon #	#1	#2	#3	#4	#5	#6	#7	#8	#9	#10	#11	#12	Top
C8	-	-	-	-	-	-	-	-	-	-	-	-	-
C10	-	-	-	-	-	-	-	-	-	-	-	-	-
C12	-	-	-	-	-	-	-	-	-	-	-	-	2929
C14	-	-	-	-	-	-	-	-	-	-	-	-	16208
C16	-	1392	-	1102	379	-	-	-	1487	-	-	-	13166
C18	-	-	-	-	-	-	-	-	-	-	-	-	9175
C20	227	447	431	401	339	283	-	303	574	-	252	147	10730
ISTD	46669	41906	30934	38395	48053	34535	40264	45541	50246	31017	39559	42042	505
C22	459	583	500	368	548	657	419	449	659	-	298	391	8467
C24	300	454	396	365	506	421	306	443	477	-	297	-	7280
C26	-	419	293	318	372	370	-	232	529	-	-	-	6607
C28	-	-	-	-	-	-	-	-	-	-	-	-	4712
C30	-	-	-	-	-	-	-	-	-	-	-	-	2732

Basic LTS													
Carbon #	#1	#2	#3	#4	#5	#6	#7	#8	#9	#10	#11	#12	Top
C8	-	-	-	-	-	-	-	-	-	-	-	-	-
C10	-	-	-	-	-	-	-	-	-	-	-	-	-
C12	431	-	-	701	-	1021	698	-	269	-	726	949	3983
C14	-	-	432	805	-	734	432	-	-	-	583	357	19723
C16	277	447	404	624	-	378	645	278	448	397	903	379	16783
C18	74	-	120	55	-	73	127	-	-	-	145	89	11789
C20	290	-	355	407	-	357	371	224	-	-	483	313	12716
ISTD	35564	30588	39844	39086	18957	48733	41718	32665	33411	29870	40795	41157	544
C22	-	-	262	303	-	388	389	-	-	-	384	203	10428
C24	-	-	285	-	-	-	-	-	-	-	346	-	8618
C26	-	-	-	-	-	-	-	-	-	-	279	-	7349
C28	-	-	-	-	-	-	-	-	-	-	-	-	4823
C30	-	-	-	-	-	-	-	-	-	-	-	-	3328

Enersperse 700													
Carbon #	#1	#2	#3	#4	#5	#6	#7	#8	#9	#10	#11	#12	Top
C8	-	-	-	-	-	-	-	-	-	-	-	-	-
C10	1807	1448	1408	1892	1837	1634	1004	1604	1845	2237	1167	2412	-
C12	442	375	333	775	701	425	207	304	414	522	400	575	4547
C14	2401	2299	2322	2448	2368	2640	1663	1287	1974	2524	2401	3243	20649
C16	2118	1272	1025	1693	1715	1311	827	1666	1431	1894	1320	2589	17203
C18	383	578	121	382	357	678	178	-41	654	1301	720	1621	8626
C20	1073	1060	921	1555	1448	1205	759	808	1258	1657	1202	2197	12677
ISTD	42772	36575	32857	45023	47717	43069	27757	34827	41002	40657	33646	53137	40774
C22	717	888	497	1104	1208	841	443	732	1249	1445	785	1592	10325
C24	616	644	579	950	939	798	439	524	775	1022	735	1393	8344
C26	576	436	415	778	670	586	363	441	548	850	637	1171	6990
C28	333	165	291	300	306	380	-	245	335	433	254	427	5416
C30	-	-	-	246	-	-	-	-	-	315	-	383	3221

- Numbers in columns refer to repeat analysis of water column samples
- Top refers to analysis of oil remaining on surface after dispersion experiment
- ISTD is the internal standard

of larger compounds that dispersants put into the water column as the weathering increases. These ratios are plotted and shown in Figure 1. Simple linear regressions were applied to the data and these show that there is an increasing trend as weathering increases. This is indicative that as the weathering increases, lesser amounts of the larger compounds are dispersed. The slopes for Corexit 9527, Dasic LTS and Enersperse 700 are the same, indicating a similar sort of composition. Corexit 9500 shows a lesser tendency to show this component separation. The composition of the water components do not change significantly as the oil weathers in the case of dispersion with Corexit 9500.

For a given oil, there is a certain amount of selectivity that occurs. Figure 2 shows the change in composition from carbon number 10 to 30 for the four different dispersants used in this study for the 15% weathered oil. Similar, if not identical, curves occur for the other oil weathering stages used in this study. Corexit 9500 shows a typical or expected selectivity for the components, where there is a decreasing amount of components in the water column as molecular size increases. The curves for Corexit 9527, Dasic LTS and Enersperse 700 show similar trends. Decane (for unknown reasons) is higher in the top sample and so is Octadecane (C18). The latter are probably concentrated at the surface because of absorption to surfactants with lipophilic chains of length 18 (eg. Oleic and Steric fatty acid surfactants). Similar effects have been noted earlier (Fingas et al., 1995).

Figure 3 shows the chromatograms of the water column sample, top sample and the originating oil. The experiment this was randomly selected from was from the fresh Federated crude test with Corexit 9500. The selectivity is often difficult to see in chromatograms, but is very slightly evident in this case. The difference in the amount of C24-C30 appears to be less in the water column sample. This shows that specific analysis such as performed here is necessary to quantify the effect.

Table 6 lists the standard dispersant effectiveness values measured during these tests. This shows that for a light and non-waxy oil such as Federated, that the gas chromatographic method and the UV/VIS method yield similar results.

## Conclusions

The series of experiments in which specific aliphatic components were analyzed in the water column and from oil remaining on the surface, shows that all components are not equally dispersed. Although the separation is slight, it is significant in that it shows that larger aliphatics are generally dispersed to a lesser degree. Furthermore, this trend is increased as the target oil weathers. That is, as the oil weathers, a lesser degree of the larger aliphatics (C24 - C30) is dispersed.

The significance of this finding is that it shows that part of the reason for poorer dispersant effectiveness with weathered and heavy oils, is the result of a lesser dispersant effectiveness with the larger compounds. However, since this effect is slight, the greatest reason for the difference in effectiveness with light and heavy oils must be the differential in effectiveness with the lighter components (<C10). This is to say that the lighter components of the oil disperse extremely well. If these are absent, the apparent dispersant effectiveness is significantly reduced.

Table 5

**Summary of Concentration Ratios**

(calculated as the average of the ratios of C10 and C12 and  
C28 and C30, if no or 0 values available, next peaks taken)

Dispersant	Concentration Ratio			
	Crude Weathering Percentage			
	0	15	28	42
Corexit 9500	1.03	1.09	1.06	1.1
Corexit 9527	1.09	1.5	0.94	1.5
Dasic LTS	0.96	0.96	1.13	1.3
Enersperse 700	0.96	1.07	1	1.31

Table 6

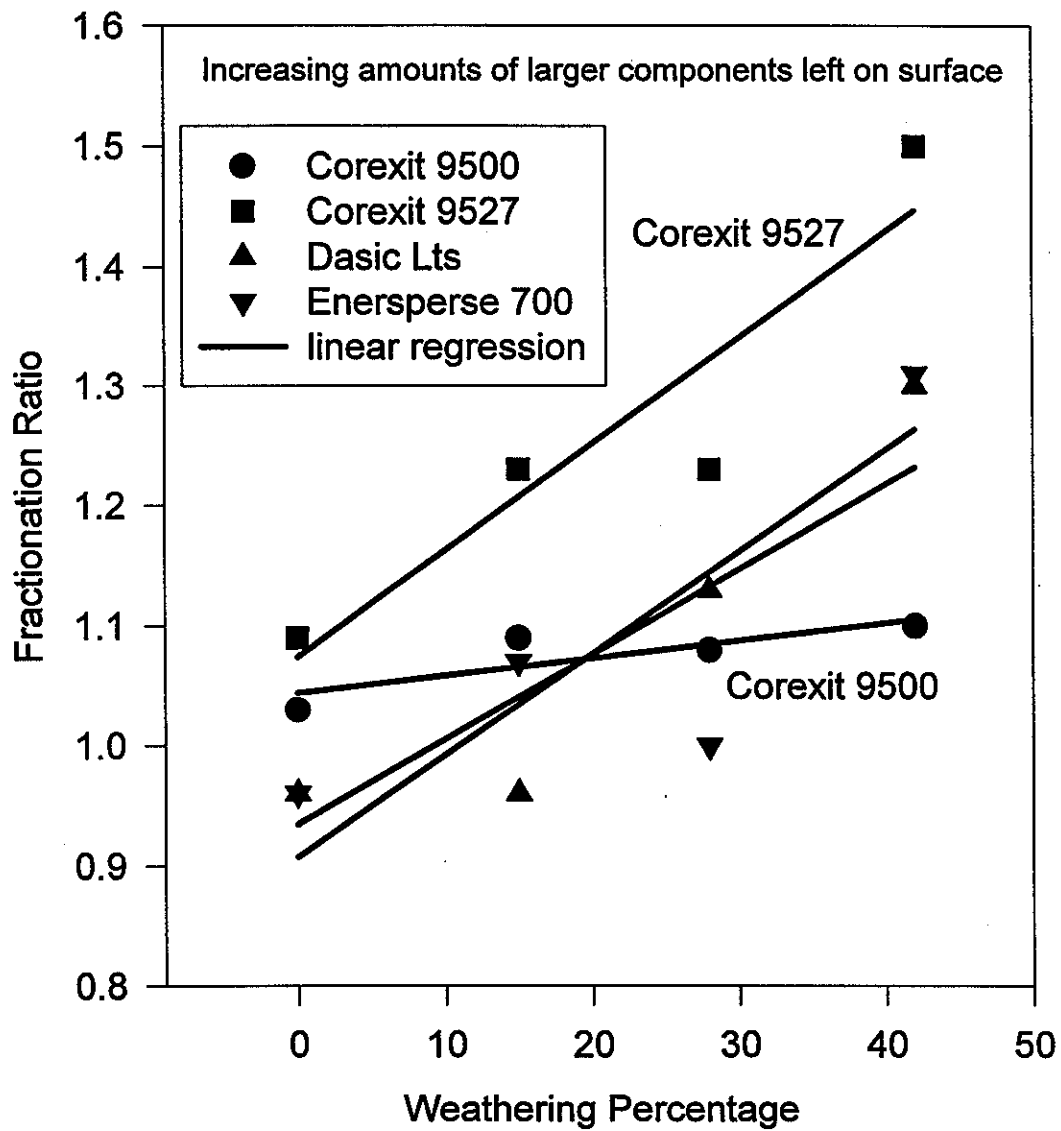
**Summary of Dispersant Effectiveness Results**

Dispersant Effectiveness in Percent  
Crude Weathering Percentage

Dispersant	0	15	28	42
Corexit 9500				
by GC-TPH	61.3	38.3	21.6	18.4
by UV/VIS	52.5	38.1	19.1	16.3
Corexit 9527				
by GC-TPH	20.4	7.5	4	1.6
by UV/VIS	17.3	9.5	5.3	4.2
Dasic LTS				
by GC-TPH	19.3	16.4	9.4	0.9
by UV/VIS	11.9	16.1	9.6	2.8
Enersperse 700				
by GC-TPH	15.1	12.6	2.5	4.4
by UV/VIS	8.3	8.5	7.9	5.8

Figure 1

## Fractionation of Components



**Figure 2 Concentration Differentials for Water and Surface**

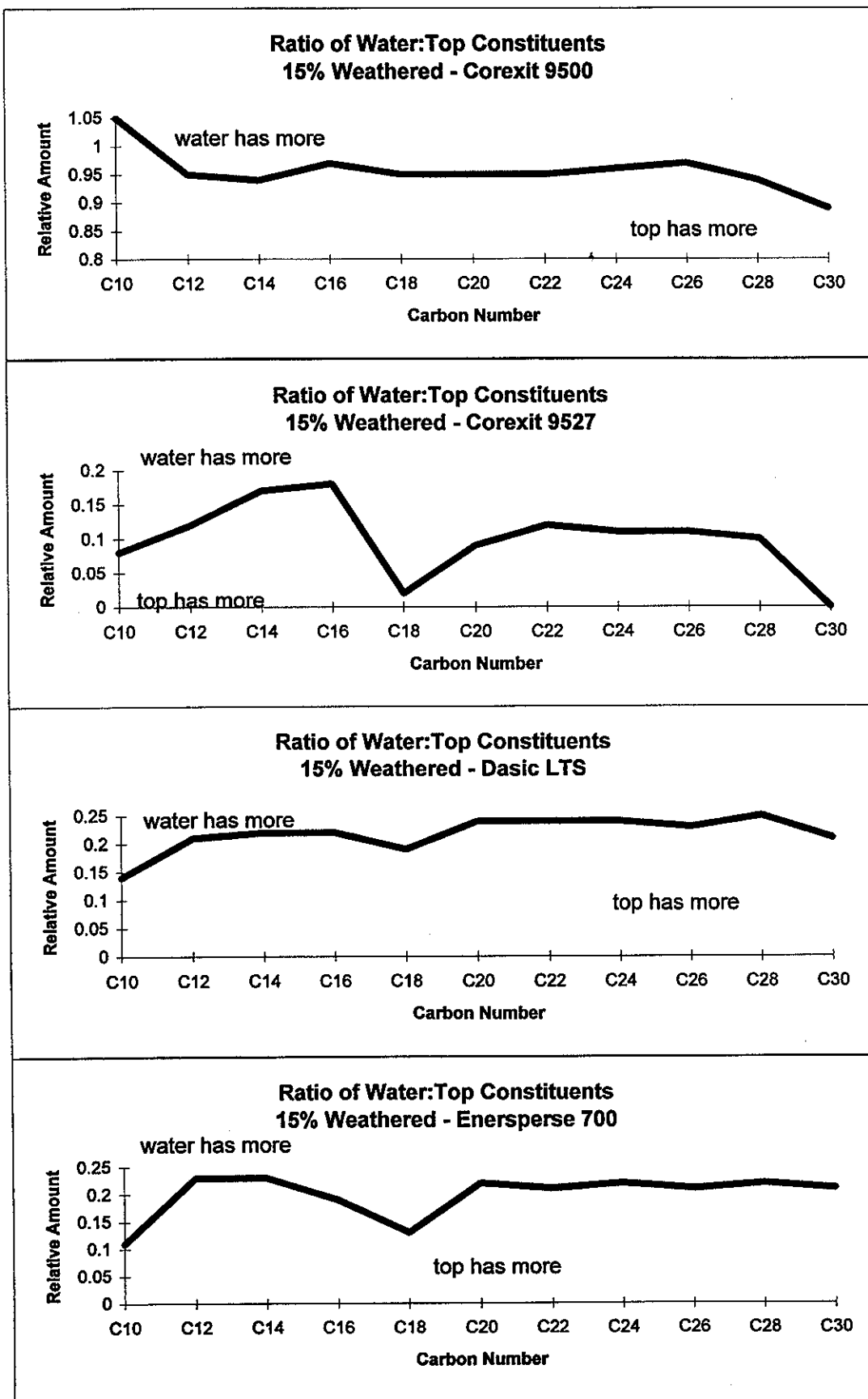
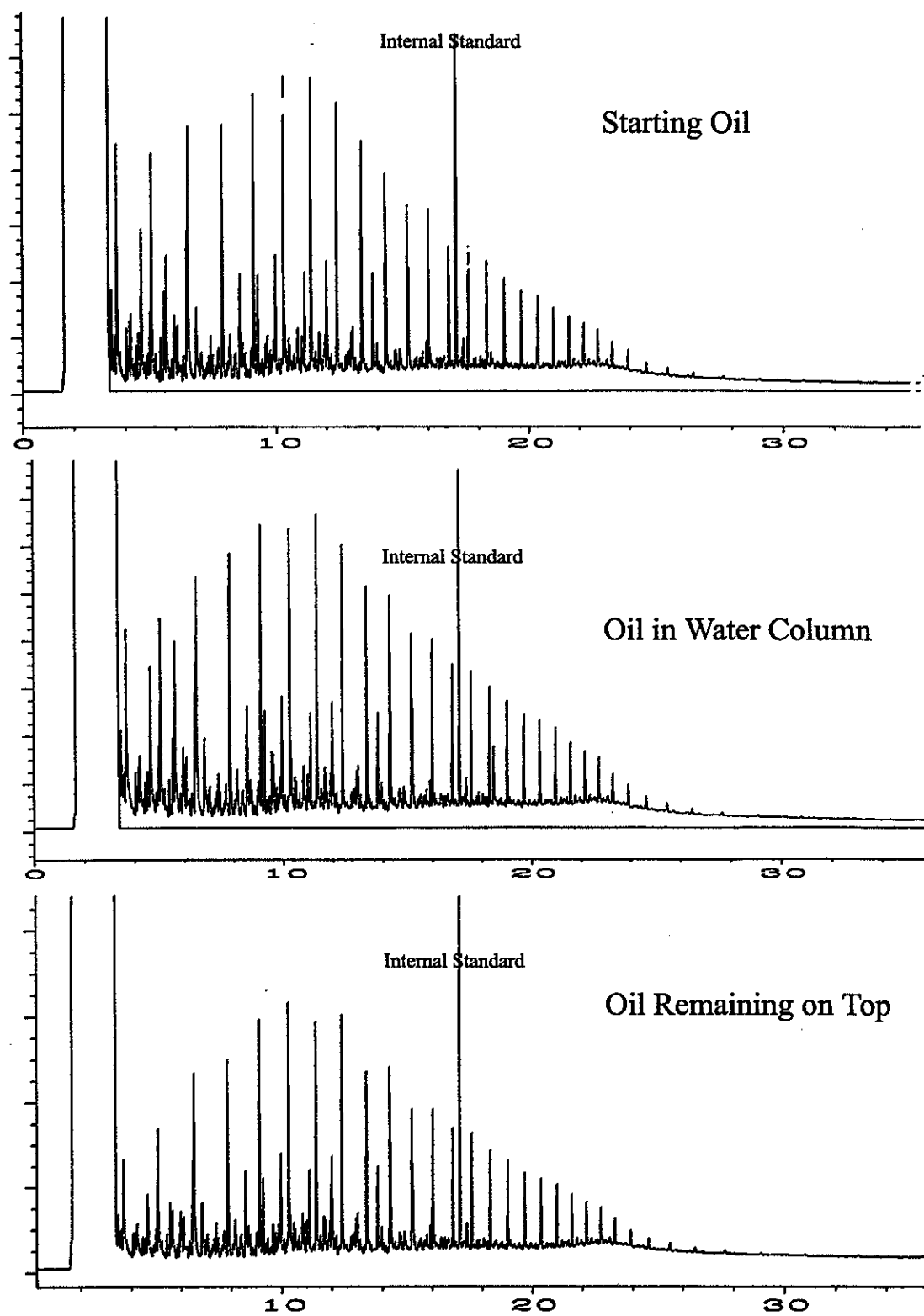


Figure 3 Chromatograms of Oil Before and After Dispersion



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